

THE CORROSION BEHAVIOUR OF Zn-4Al (AC43A) AND Si_p/(Zn-4Al) COMPOSITES IN AN ARTIFICIAL SEA WATER

A. A OMAR AND A. KANDIL

Mining and Petroleum Engineering Department, Faculty of Engineering,
Al-Azhar University, Nasr City, Cairo, EGYPT

(Received December 10, 2005 Accepted January 22, 2006)

ABSTRACT– The corrosion behavior of the cast Zn-4Al and Si/(Zn-4Al) alloys when attacked by 3.5% NaCl solution at different temperatures, 31, 40, 50, and 60 °C was investigated. The Tafel intercept logarithmic polarization methods was utilized for determining the corrosion parameters. Some corrosion kinetic and mechanistic parameters have been studied in the absence and presence various concentration of K₂CrO₄. The study indicated that the percentage inhibition efficiency increased with the increase of the inhibitor concentration and decreased with increase of solution temperature. The activation energy of corrosion increased by the increase of both the corrosion rate and temperature. The addition of Si particles into Zn-4Al can greatly improve the corrosion resistance and has a significant effect on the Tafel polarization measurements. The corrosion resistance increase with increasing the volume fraction of Si-Particles.

INTRODUCTION

Commercial zinc and zinc-aluminium alloys (ZA) have been used extensively in industry. This attributed to their excellent fluidity, castability and good mechanical properties [1,2]. The zinc alloy excellent mechanical properties rendered them an attractive substitute for cast iron and copper alloys in many structural and pressure-tight applications. The zinc costs less than copper therefore zinc alloys have a distinct cost advantage over copper base alloy [3-5]. The main areas of alloy's application are transportation industry, fuel-pumps bodies, pressure-tight, pulleys, electrical fitting and hardware components [6] One of the main disadvantages of these alloys is the poor wear resistance, which in turn, reduces their service life [2,5]. The ease of machining of zinc and its inherent corrosion resistance give it advantages over cast iron. In situations where zinc plating or some other protective finish is required to prevent atmospheric corrosion of cast iron, direct substitution of zinc foundry alloy may be possible [7-10].

Among the zinc-aluminium alloys used for coating to protect steel and iron from corrosion, Zn-4Al (AC43A), and Zn-55Al alloys have attracted particular interest in recent year. Aluminium addition to the zinc bath is deliberately added to form zinc coated galvanized steel. These additions have been made to (1) improve the luster or reflectivity of coating, (2) reduce oxidation of the zinc bath, (3) to obtain ductile coating by suppressing the formation of brittle Fe –Zn phases [11]. By the addition of

a high melting elements such as silicon to zinc-aluminum alloy to produce zinc-matrix composites with improved mechanical properties, wear resistance, fluidity and good thermal stability are achievable [3,12]. Very few data is available in the literature showing the effect of the alloying elements such as silicon on zinc-aluminum alloys corrosion resistance.

The aim of this study is to investigate the effect of different volume fraction percent (vol.%) of Si_p , inhibitor, and the temperature on the corrosion behaviour of Zn-4Al (AC43A) and Si_p /Zn-4Al in 3.5% NaCl using polarisation measurements.

EXPERIMENTAL PROCEDURE

Materials Preparation

The Zn-4Al (AC43A) alloy and Zn-4Al reinforced with 5, 10, and 15 vol.% Si_p were prepared by liquid metallurgical route in a permanent steel mould (30 mm diameter, and 120 mm height). Using an electrical resistance heated furnace of 8 kW power and three-blade graphite stirrer driven by a variable speed motor. The graphite blade stirrer has a diameter of 56 mm and is 14-mm thickness. Both the crucible and stirrer has been coated with zircon mold and then washed before each experiment. The temperature of the melt was measured by using a Ni-CrNi thermocouple

High purity zinc (99.9%), commercially pure aluminium (99.8%), electrolytic copper (99.9%), and Al-Si master alloy (50wt% Si) were used for the production of these alloys.

According to ASTM composition, the Zn-4Al (AC43A) alloy was prepared by melting 650 g Zn, 30 g Al, and 20 g electrolytic copper in aluminium oxide crucible at 650 °C and held at this temperature for 20 minutes. The molten metal was poured into a steel mold.

The metal matrix composites of Zn-4Al reinforced with 5, 10, and 15 vol.% Si_p were prepared using two electrical resistance furnace. The mechanical stirring was applied to mix different amounts of Si_p with the molten metal of control alloy. The main constituents of the un-reinforced alloy (AC43A) were maintain constant as 650 g zinc, 30 g pure aluminium, and 20 g pure copper. The Al-Si master alloy contains 50 wt.% Si of different amounts i.e. 30, 45, 60 g were heated for semi solid state at 700 °C, then held for 20 minutes and hand stirred with graphite rods. The molten metal of Zn-4Al (control alloy) was poured into semi solid slurry Al-Si (50wt% Si). The mixture of the melt was being stirred at 800 r.p.m., then the mixture of the mould was poured into permanent mould (30 mm diam. and 120 mm height).

The cast billets of the (AC43A)/5, 10 and 15 vol.% Si_p as well as the matrix alloy Zn-4Al for microstructure examination were sectioned from short transverse direction, grinding on a series of SiC emery papers (320, 500, 800, 1000, 1100 grit) and followed by polishing on a series polishing cloth with diamond paste of 6, 3, 1 μ m. After that, the samples were etched with (0.5% HF), to reveal the morphology and structure characteristics. Optical microscopy was done on ground and polished specimen cross-sections to determine the volume fractions of Si_p in the matrix. This was done by point counting, using a 10 x 10 grid on 20 different areas of each cross-section. The smallest and largest matrix volume fractions were discarded and averages were calculated from the remaining values according to the ASTM Standard E-562 [13]. The composition of

the AC43A(zinc alloy) was determined by Schmieden von Damaszennerstahl und Kupfer-Zink-Legierung, Augsburg (Germany). The chemical compositions of Zn-4Al (AC43A) alloy are given in **Table 1**.

For corrosion test, rectangular specimens were used. It was covered with plastic sliver tape to achieve a total surface area of 1.9 cm² (0.295 in²). The actual dimensions of the working electrode samples 1cm (0.394 in) in width and 1.9 cm (0.748 in) in length were made for the purpose of determining the corrosion rate and corrosion parameters. Solutions were prepared using distilled water and A.R. grade chemicals. The test specimens were handled in 3.5% NaCl containing different concentrations of potassium chromate ranging from 0.025 to 0.100 M at 31, 40, 50, and 60°C. All test specimens were polished emery paper number 400 and finished to 800 grit and then degreased by acetone and handled with freshly prepared electrolyte solution. The electrochemical tests were performed using a Corrosion Measurement System (Potentiostatic/Galvanostatic-273A) with Ag/AgCl electrode and platinum foil (Pt) were used as reference and counter electrode. The corrosion current (I_{corr}), corrosion rate and percentage inhibition (η) for inhibitor at different concentration and temperature have been evaluated employing Tafel intercepts logarithmic polarization technique [14-20]. All experiments were performed in a glass corrosion cell containing 100 ml of test solution.

Table 1: Chemical analysis of zinc matrix alloy Zn-4Al (AC43A) (wt.%).

Al	Cu	Fe	Cd	Sn	Ti	Pb	Zn
4.23	2.79	0.741	0.14	0.004	0.0018	0.0024	bal.

RESULTS AND DISCUSSIONS

Microstructural Characterizations

The Zn-4Al, which is near eutectic point in the Zn-Al phase diagram in **Fig. 1**. The microstructure of the Zn-4Al is characterized by a two phase structure, a zinc rich eta (η) proeutectoid phase surrounded by the eutectic type phase consisting of beta (β) aluminium and η zinc lamella (**Fig. 2**). However, the microstructure can vary depending upon cooling rate [21].

In the early stages of solidification, proeutectic zinc particles nucleate first and the solidification of the eutectic matrix proceeds from these particles. The amount of proeutectic was calculated to be 18 % [22]. These result indicate nonreciprocal nucleating characteristics, i.e. one primary phase, but not vice versa, and the nucleation characteristics in off-eutectic Zn-Al alloy have been detailed [22].

Polarization Measurements

The percentage inhibition efficiency, and corrosion rate in the presence and absence of inhibitor (K_2CrO_4) at different concentrations for different specimens are given in **Table 2**. The percentage inhibition efficiency were calculated as:

$$I.E = \frac{I_{corr}^{(blank)} - I_{corr}^{(inhib)}}{I_{corr}^{(inhib)}} \times 100 \quad (1)$$

Where, $I_{\text{corr}}^{(\text{blank})}$ and $I_{\text{corr}}^{(\text{inhib})}$ are the corrosion current densities ($\mu\text{A}/\text{in}^2$) in absence and presence of the inhibitor, respectively.

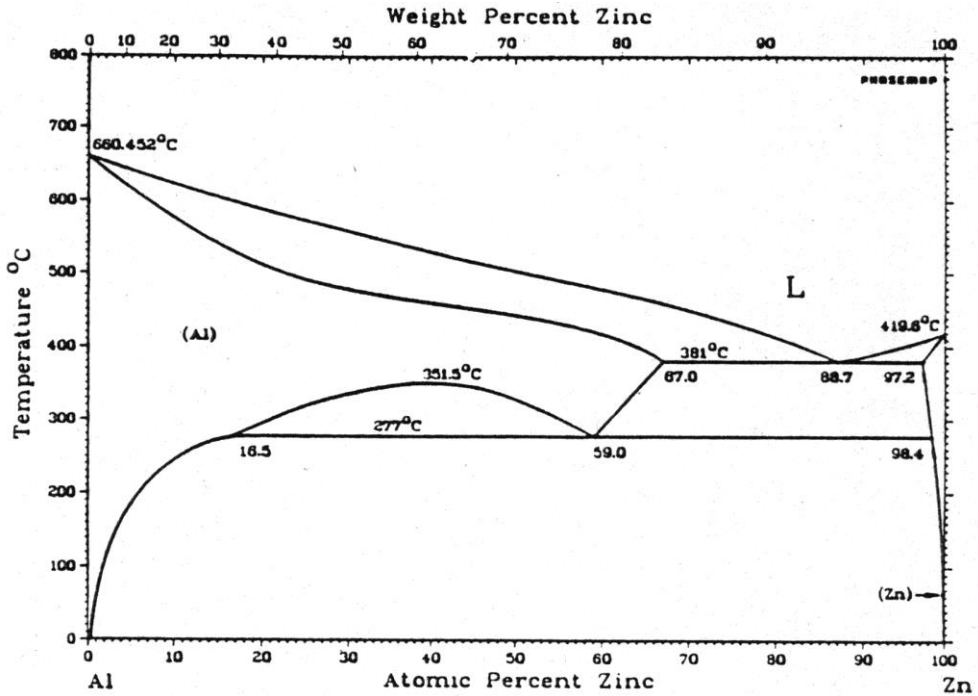


Fig. 1: Equilibrium phase diagram of Al-Zn alloy.

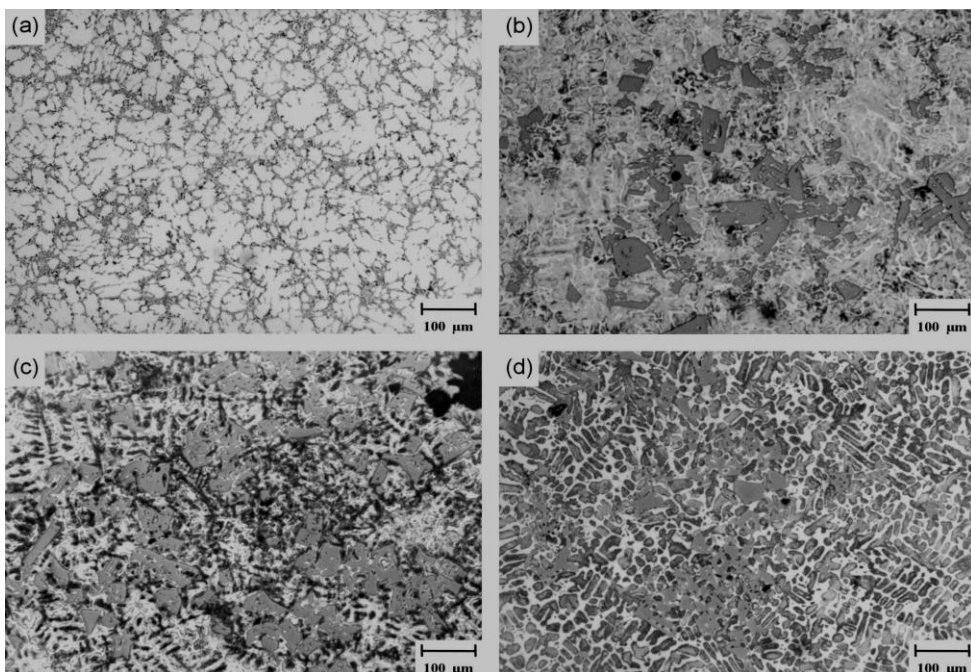


Fig.2: Micrograph of as-cast Zn-4Al (AC43A) alloy reinforced with Si particles, a) un-reinforced, b) 5 vol.%, c) 10 vol.%, d) 15 vol.%.

It is evident from **Table 2** that the inhibition efficiency increases with increasing inhibitor concentration. The maximum inhibitor efficiency (69.83%) was reached at maximum inhibitor concentration (0.100 M K_2CrO_4 without an addition of Si_p to Zn-4Al alloy. The addition of silicon particles by 5, 10, and 15 vol. % into the Zn-4Al alloy decreased the corrosion rate and corrosion current density (I_{corr}). This may be attribute to the formation of strong intermetallic compounds between Si_p and elements of the matrix. Results show that the current corrosion lowering and slightly decreased in E_{corr} with increasing inhibitor concentration of K_2CrO_4 bring out the fact that for inhibitor being adsorbed on the metal surface and suppresses metal dissolution and reduction reactions because of which the corrosion rate decrease appreciably [23-26]. The inhibition efficiency and corrosion rate of Zn-4Al alloy reinforced with 5 vol.% Si_p in 3.5% NaCl in presence and absence various concentration of K_2CrO_4 at different temperature are shown in **Table 3**. It can be seen that the maximum inhibition efficiencies were obtained at room temperature; also decrease in inhibition efficiency is observed with temperature increase. It seems that with an increasing in temperature the time lag become shorter for the process of adsorption and desorption of the inhibitor molecules on the metal surface, resulting in a decrease inhibition efficiency [20]. In general, the percentage inhibition efficiency in 3.5% NaCl at each of the four test temperatures increases in the order: 0.025, 0.050, 0.075, and 0.100 M K_2CrO_4 , while the corrosion rate decreases with increasing inhibitor concentration and increases with increasing temperature .

The effect of increasing volume fraction percent of Si_p on the anodic and cathodic polarization curves (Tafel plot) for Zn-4Al alloy in 3.5 % NaCl at different concentration of K_2CrO_4 are illustrated in **Fig. 3**. It can be seen that the addition of Si_p into Zn -4Al production alloy has significant effect on the Tafel polarization measurements. Tafel curves of the materials tested in the as cast and reinforced are shown in Fig 3 (a, b, c, d, and e). The unreinforced alloy (Zn-4Al) showed no better performance than the reinforced alloys which contain 5, 10, and 15 % vol % Si_p . Polarization measurement showed one cathodic reaction representing the reduction of hydrogen ions, and one anodic reactions at the more negative potential represent the anodic oxidation of certain phases **Fig. 3**.

After an addition of volume percent of Si_p , the E_{corr} of the composite showed shifts to the positive direction which could be related to an increase in volume fraction of silicon phase involved in that reaction, **Fig. 1 (a, b, c, d and e)**. The reinforced alloys have the lowest I_{corr} , while the unreinforced alloy was more than five times higher Fig 3 (a, b, c, d, and e). Corrosion rate by Tafel polarization measurement showed significant difference since it varied between 15.4×10^{-3} to 10.03×10^{-3} mpy for (a) at 0.0 M K_2CrO_4 ; 38.10×10^{-3} to 8.49×10^{-3} mpy for (b) at 0.025 M K_2CrO_4 ; 28.06×10^{-3} to 6.09×10^{-3} mpy for (c) at 0.05 M K_2CrO_4 ; 20.10×10^{-3} to 5.4×10^{-3} mpy for (d) at 0.075 M K_2CrO_4 and 15.5×10^{-3} to 3.98×10^{-3} mpy for (E) at 0.100 M K_2CrO_4 , the lowest values for the reinforced alloy contain 5, 10, and 15 vol % Si_p at high concentration of K_2CrO_4 .

The activation energy of corrosion of Si_p /(Zn-4Al) alloy contains 5 vol. % Si_p in 3.5% NaCl was calculated from the equation:

Table 2: Corrosion parameters obtained from anodic and cathodic Tafel plot for Zn-4Al and Zn-Al reinforced with different volume fraction of Si_p in presence and absence various concentration of K₂CrO₄ at room temperature.

Volume percentage of Si _p (%)	K ₂ CrO ₄ Conc. (M)	β _a *10 ⁻³ (Ag/AgCl) (V)	β _c *10 ⁻³ (Ag/AgCl) (V)	E _{corr.} Ag/AgCl (V)	I _{corr.} (μA)	Corrosion Rate*10 ⁻³ (mpy)	Inhibition Efficiency (η). (%)
0.00	0.00	85.0	111.6	-1.08	36.16	51.4	----
	0.025	189.2	172.3	-1.00	26.80	38.10	25.88
	0.050	167.5	37.4	-0.980	19.78	28.06	45.30
	0.075	149.5	183.3	-0.960	14.75	20.10	59.21
	0.100.	108.0	149.2	-0.880	10.91	15.50	69.83
5.0	0.00	34.4	953.1	-0.965	15.55	30.40	----
	0.025	134.5	178.3	-0.463	12.25	23.10	21.22
	0.050	298.0	268.8	-0.330	9.77	20.70	37.17
	0.075	429.3	239.1	-0.332	7.50	14.66	51.77
	0.100	278.6	105.8	-0.310	5.55	11.50	64.31
10.0	0.00	54.6	116.6	-1.06	6.69	17.98	-----
	0.025	58.1	318.0	-0.977	5.60	14.01	16.29
	0.050	232.6	84.0	-0.960	4.65	10.14	30.49
	0.075	83.8	132.0	-0.947	3.81	8.33	43.05
	0.100	181.1	133.9	-0.865	2.82	6.17	57.85
15.0	0.00	24.0	108.8	-1.05	2.88	10.63	----
	0.025	107.4	227.3	-0.902	2.56	8.49	11.11
	0.050	2.0	279.3	-0.901	2.18	6.09	24.31
	0.075	247.0	181.6	-0.890	1.94	5.41	32.64
	0.100	223.4	185.0	-0.850	1.43	3.98	50.35

Table 3: Inhibition efficiency and corrosion rate for specimen of Zn-4Al composite reinforced with 5% vol.% Si_p in 3.5% NaCl in presence and absence various concentration of K₂CrO₄ at different temperature.

Vol. Fraction of Si _p %	K ₂ CrO ₄ Conce. (M)	Inhibition efficiency, %				I _{corr.} , uA				Corrosion rate, mpy			
		31 °C	40 °C	50 °C	60 °C	31 °C	40 °C	50 °C	60 °C	31 °C	40 °C	50 °C	60 °C
5	0.00	-	-	-	-	15.55	22.08	31.33	44.48	30.40	42.89	61.25	86.98
	0.025	21.22	20.74	19.85	18.05	12.25	17.50	25.11	36.45	23.50	33.50	49.11	71.31
	0.050	37.17	31.90	30.07	27.29	9.77	15.15	21.28	32.34	20.15	28.90	42.84	62.45
	0.075	51.77	51.00	48.52	44.02	7.50	10.65	16.13	24.90	14.66	21.15	31.53	46.50
	0.10	64.31	62.86	60.28	57.81	5.55	6.41	10.12	18.77	10.67	15.48	23.21	35.55

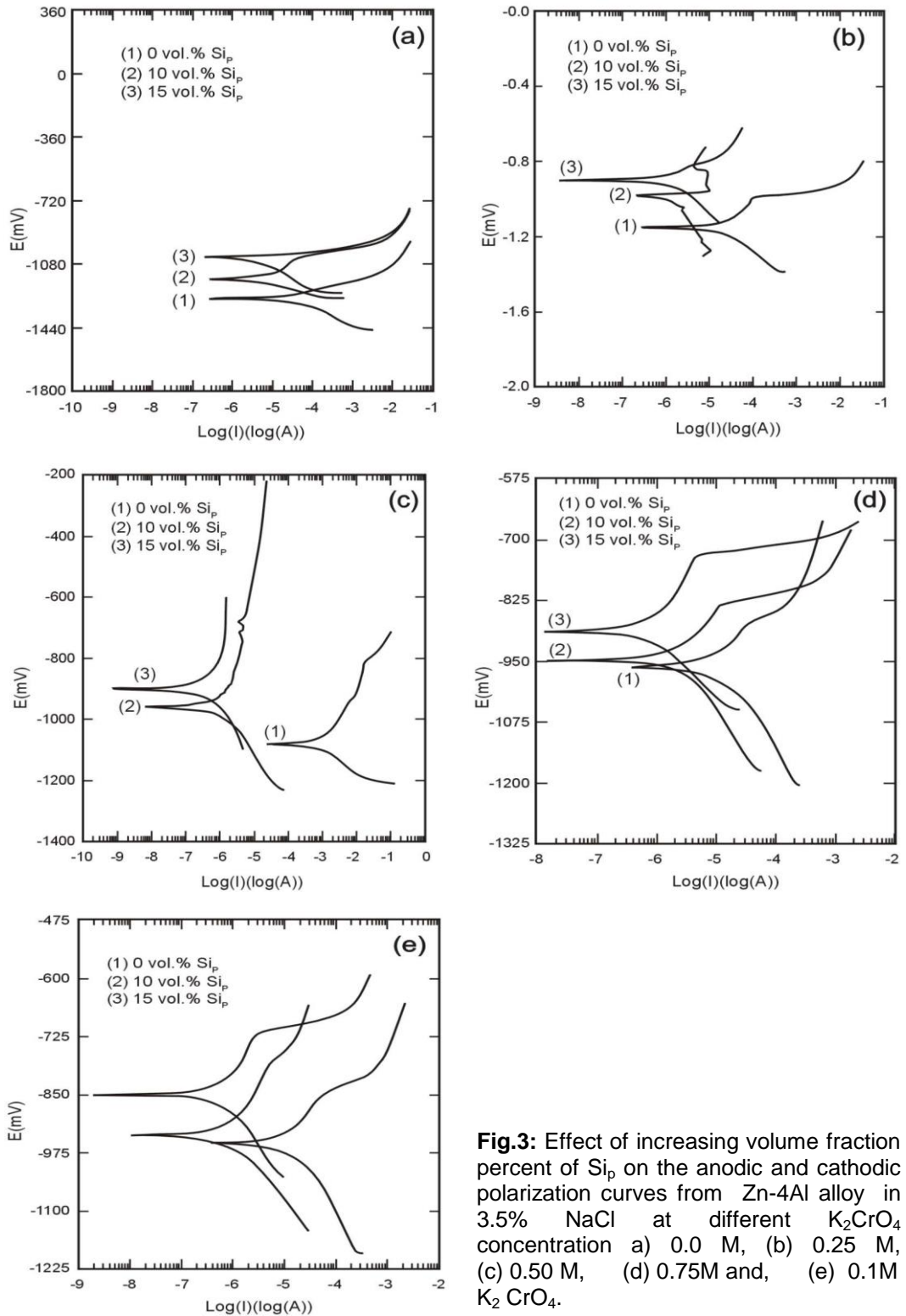


Fig.3: Effect of increasing volume fraction percent of Si_p on the anodic and cathodic polarization curves from Zn-4Al alloy in 3.5% NaCl at different K_2CrO_4 concentration a) 0.0 M, (b) 0.25 M, (c) 0.50 M, (d) 0.75M and, (e) 0.1M K_2CrO_4 .

$$\text{Log} (K_2/K_1) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

Where K_1 and K_2 are the rate constants at temperature T_1 and T_2 , respectively. R is the gas constant and E_a is the activation energy. The activation energy E_a for $\text{Si}_p/(\text{Zn-4Al})$ composite contains 5 vol.% Si_p in 3.5% NaCl with and without inhibitor was calculated from experimental data and tabulated in **Table 4**. It is observed that, the activation energies from inhibited NaCl were 7.16, 7.22, and 7.5 K.Cal.mol⁻¹ for the temperature ranges 31-40, 40-50, and 50-60°C respectively. In general, the activation energy of this composite alloy increases with increasing inhibitor concentration as well as temperature range. This may be indicative of the fact that the number of adsorbed inhibitor molecules on the metal surface increase. Hence, the maximum activation energies were obtained at high inhibitor concentration in all temperature range. The values of E_a were also calculated from slopes of $\log K - T^{-1}$ plots (**Fig. 4**) and show in **Table 4**. It is important to note that within the range of temperatures studied, the activation energy obtained concerning the effect of temperature on the corrosion rate.

Table 4: Activation energy of corrosion, E_a for Zn-4Al composite reinforced with 5 vol. % Si_p in 3.5% NaCl with and without inhibitor.

Vol. Fraction of Si_p %	K_2CrO_4 Conce. (M)	E_a from experimental data, (k. cal. mol ⁻¹)			E_a from graph, (k. cal. mol ⁻¹)
		304-313 °K	313-323 °K	323-333 °K	
5	0.00	7.16	7.22	7.50	7.47
	0.025	7.45	7.69	7.97	7.70
	0.05	7.58	7.91	8.06	7.86
	0.075	7.70	8.02	8.30	8.01
	0.10	7.82	8.14	8.57	8.33

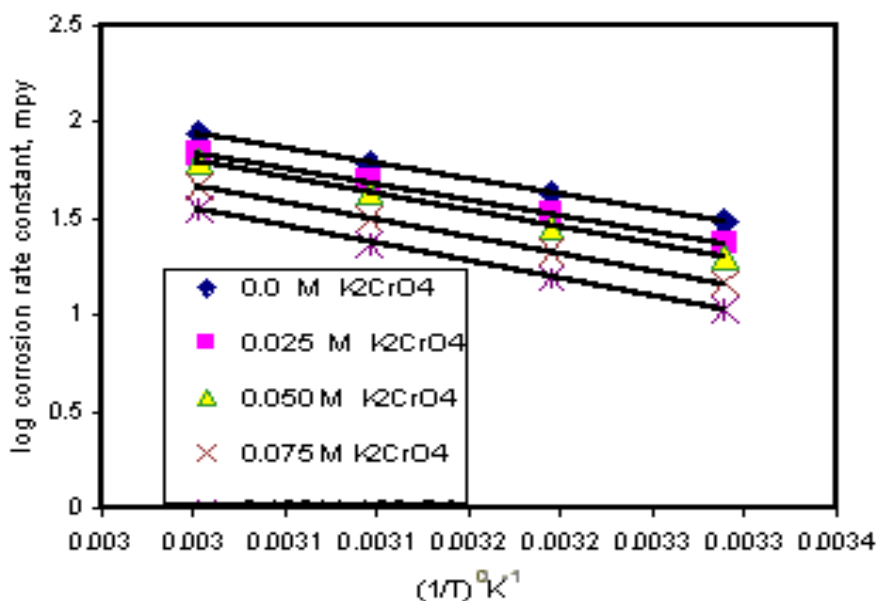


Fig. 4: log the corrosion rate constant K as function of reciprocal temperature for Si_p (Zn-4Al)/ composite in 3.5% NaCl containing addition of K_2CrO_4 .

CONCLUSION

Based on the results obtained in the investigation, the following conclusion emerged:

1. Liquid metallurgical technique was successfully used to introduce Si_p particles reinforced Zn –4Al matrix composites.
2. The addition of Si_p particles into Zn –4Al has a marked effect on the corrosion rate .The corrosion rate decreased with increase volume fraction of Si-particles.
3. The inhibition efficiency of potassium chromate for Si_p /(Zn –4Al) composites containing 5 vol.% Si_p in 3.5 % NaCl at 31, 40, 50, and 60 °C increases in the order of 0.025, 0.050, 0.075, and 0.100 M K_2CrO_4 .
4. The inhibition efficiency of this composite decreased with the increase of temperature in the range 31-60 °C
5. In general, the activation energy of corrosion of Si_p /(Zn –4Al) composite containing 5 vol % Si_p in 3.5 NaCl increase with increasing concentration of K_2CrO_4 .
6. The activation energy obtained from the Arrhinious plot shows good agreement with those calculated from experimental results.

REFERENCES

- [1] Z.Q. Li, S.Y Zhang and B. Y. Wu: Materials Sci. and Techol. 17 (2001) p.465
- [2] B: K, Parasad , A.K. Patwardan and A. H. Yegeneswaran: Wear 199 (1996) P.142
- [3] H. Akbulut and A. Turk: Z. Mezallkd 91 (2000) P. 5
- [4] T. Savaskan , M. Aydin and H. A.. Odabasiglu: Material Sci. and Technol. 17 (2001) P. 681
- [5] P. Deleneuveville: Wear 105 (1985) P. 283
- [6] E. T. Kubel: Adv. Mater. Proc.132 (1985) P. 43
- [7] K. Tano: Nippon Steel technical Report. No.25 April (1985) P.29
- [8] J: Short Mackowaik: Int. Met. Reviews (1979) P.1
- [9] R. W. Richards, R.D. Jones, P. D. Clements, and H. Clarke: Int. Mater. Reviews (1994) P.191
- [10] H. E. Townsend: Materials Selection and design, oct. (1991) P. 60
- [11] R. Marder: Progress in Materials Sic. 45 (2000) P. 191
- [12] M. D. Hanna, J. T. Carter and M. S. Rachid: Wear 203 (1997) P. 11
- [13] H. E. Exner, O. Pall , and K. Dieser: Park. Metallogr. 30 (1993) P. 216
- [14] W.A. Metwally: Aluminum, 71, Jahrgang, 2, (1995) P 211-214.
- [15] F.A. Champion: Corrosion Testing Procedure, Wiley Great Britain, 190 (1952) P16.
- [16] H.h. Uhlig: Corr and Corr Cont, Wiley USA (1967) P 28.
- [17] S. Glasstone: An Introduction To Electrochemistry, D. Van Nnstrant Inc New York, (1962).
- [18] G. Joseph, and R. Perret: Corrosion Sic., 7(1967) P533.
- [19] Green and Fontana: Corrosion of Metals, Mc Graw Hill, New York (1964) P143.
- [20] P.N.S. Yadav: British Corrosion Journal, Vol. 34 No. 1 (1999) P 51-52.

- [21] AF Skenazi, D. Davin, D. Coutsouradis and FD. Goodwin: Proceeding of 1st International Conferance on Zinc Coated Steel , Munich, London: Zinc Development Association 1985
- [22] S.T. Bluni, M.R. Notis and A.R. Marder: Acta Metall, Mater. 43 (1995) P. 1775
- [23] Meena, Shankar Lal, Goyal, Praveen, Sharma Alka, I.K. Sharma, and P.S.Verma: Bulletin of Electrochemistry 19, September (2003) P 405-412.
- [24] M.A. Quaraishi, and J. Rawat :IX NH Conv of Electrochemists (NCE-IX) Souv and Abs, (Surat), (Nov. 1999).
- [25] J. Amalrj, and M. Sundaravadivelu: IX NH Conv of Electrochemists (NCE-IX) Souv and Abs, (Surat), (Nov. 1999).
- [26] J. J. Vora, J.C. Vora, and V.H. Shan: Trans SEAST, 32 (1997) P 54.

سلوك التآكل لسبيكة الزنك-4الومنيوم وسبائك المواد المركبة من السليكون ، الزنك-4الومنيوم في ماء البحر المصنع

يهدف البحث بالدراسة والتحليل لخاصية التآكل لسبيكة الزنك - 4 الومنيوم وسبيكة المواد المترابطة للزنك-4 الومنيوم المقواة بحبيبات السليكون ذو النسب الحجمية المختلفة 5 و10 و15% (كسر حجمي) في محلول ماء البحر المصنع (3.5% كلوريد الصوديوم) عند درجات حرارة مختلفة. باستخدام الطرق الكهرو كيميائية مع دراسة العوامل المؤثرة على حركة وميكانيكية التآكل والتمثلة في كثافة تيار التآكل , جهد التآكل , ومخطط ميلى الأنود والكاثود للسبائك المقواه بحبيبات السليكون والسبيكة الغير مقواه. وقد وجد أن إضافة السليكون للسبيكة زنك-4 الومنيوم أدى إلى زحزحة جهد التآكل في الاتجاه الموجب مما ترتب عليه زيادة مقاومة السبيكة للتآكل وخفض قيمة تيار التآكل. ولقد أوضحت النتائج أن كثافة المثبطات تزيد بزيادة تركيزها وتقل بزيادة درجة الحرارة ومن التجارب العملية تم تحديد طاقة التنشيط في وجود كرومات البوتاسيوم ذات التركيزات المختلفة. وقد وجد أن هذه الطاقة تزداد بزيادة كل من معدل التآكل ودرجة الحرارة .